OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0470-P00003

R&T Code NR 33359-718

Technical Report No. 89

The Behavior of Microring and Microdisk Electrodes

by

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Prepared for publication in J. Electroanal. Chem.

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July 15, 1988

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release and sale. Distribution unlimited.
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report No. 89	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION University of Utah 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Henry Eyring Building Salt Lake City, UT 84112	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-83-K-0470-P00003
8c. ADDRESS (City, State, and ZIP Code) Chemistry Program, Code 1113 800 N. Quincy Street Arlington, VA 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
The Behavior of Microring and Microdisk Electrodes

12. PERSONAL AUTHOR(S)
M. Fleischmann and S. Pons

13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 9/87 TO 7/88	14. DATE OF REPORT (Year, Month, Day) July 15, 1988	15. PAGE COUNT 20

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Microelectrodes, Mass transport

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Attached.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Stanley Pons	22b. TELEPHONE (Include Area Code) (801)581-4760

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION

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J. Electroanal. Chem., 0 (1987) JEC08941
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE BEHAVIOR OF MICRODISK AND MICRORING ELECTRODES *

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(Received 2nd December 1986)

ABSTRACT

An exact analysis of diffusion to microdisk and microring electrodes is presented for steady-state conditions and for the assumptions of constant concentration over the surface of the disk and constant flux over the surface of the ring electrodes. Mass transfer to ring electrodes is progressively enhanced by reducing their thickness which also reduces changes in concentration with position over the surface of the ring as well as the differences between the mass transfer coefficient for the constant concentration and constant flux conditions. Thin rings are therefore recommended for investigations of electrode kinetics.

INTRODUCTION

Studies of fast electrochemical kinetics traditionally have been accomplished by the use of transient and ac perturbation techniques, such as those pioneered by Professor Don Smith. Electrochemical measurements at conventionally sized electrodes, however, invariably contain the effects of capacitative charging of the electrical double layer. In addition, ohmic losses at these electrodes can be considerable when high currents flow in the cell, such as those which occur in potential step experiments, or when the resistance of the electrolyte solution is high. There has, therefore, been a recent movement toward the utilization of ultramicroelectrodes for electrochemical measurements; the high mass transport rates, small currents, and low surface areas which characterize these devices provide distinct advantages over measurements at conventionally sized electrodes. High mass transport rates, due to the essentially spherical diffusion field surrounding these structures, give rise to unchanging concentration profiles in short times. This facilitates the study of fast electrochemical kinetics under steady state conditions. The small currents flowing in the cell reduce ohmic losses, and allow measurements to be made in highly resistive

* Dedicated to the memory of Don Smith.
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0022-0728/87/$03.50

media. The low surface areas of these devices reduce double-layer charging to very small proportions. We discuss in this paper the behavior of two commonly used ultramicroelectrode geometries.

Most previous discussions of the behavior of microdisk (e.g., see refs. 1–10) as well as recent discussions of the behavior of microring [11,12] electrodes have been based on attempts to solve and interpret the time-dependent diffusion problem in the cylindrical coordinate system (or else using coordinates derived from this system):

$$\frac{\partial c}{\partial t} = \frac{D\partial^2 c}{\partial r^2} + \frac{D}{r}\frac{\partial c}{\partial r} + D\frac{\partial^2 c}{\partial z^2} \tag{1}$$

The original motivation was the examination of the behavior of comparatively large electrodes affected by "edge effects." However, a major advantage of the use of microelectrodes is the ability to use these structures in the study of fast electrode reactions [e.g. 13,14] (and of fast reactions in solution coupled to electrode reactions [15,16]) under steady-state diffusion conditions. As the algebraic or numerical calculation of the time-dependent response in the cylindrical coordinate system is demanding, it is therefore always worthwhile to explore whether there is a steady-state solution for any given electrode geometry. This is certainly the case for spherical (or hemispherical) electrodes and one would expect this to hold also for microdisks and microrings since these electrodes are surrounded by essentially spherical diffusion zones. In this paper we therefore explore the direct solution of

$$\frac{\partial^2 c}{\partial r^2} + \frac{\partial c}{r\partial r} + \frac{\partial^2 c}{\partial z^2} = 0 \tag{2}$$

for these electrode systems.

MICRODISKS

The solution of analogous problems in heat conduction and electrical potential theory is well known [e.g. 17–20] *. As we shall use the known properties of

* Lord Kelvin refers to an experimental determination of the ratio of the capacitance of a sphere and a disk as being 1.57 (i.e. $\pi/2$). We quote Lord Kelvin:

"My authority for this statement is the following entry which I find written in pencil on an old memorandum book:

PLYMOUTH, Mond. July 2, 1849

"Sir William Snow Harris has been showing me Cavendish's unpublished MSS. put in his hands by Lord Burlington, and his work upon them; a most valuable mine of results. I find already the capacity of a disc (circular) was determined by Cavendish as 1/1.57 that of a sphere of same radius. Now we have

$$\text{capacity of disc} = \frac{\int_0^a \frac{r\,dr}{(a^2-r^2)^{1/2}}}{\int_0^a \frac{dr}{(a^2-r^2)^{1/2}}} = \frac{a}{\pi/2} = \frac{a}{1.571}!$$

It is much to be desired that those manuscripts of Cavendish should be published complete; or, at all events, that their safe keeping and accessibility be secured to the world."

discontinuous integrals of Bessel functions [21] to derive a solution for mass transfer to thin ring electrodes, we outline briefly the solution for a disk, $0 < r < a$ maintained at a constant concentration c^s, with zero flux over the surface $r > a$ i.e.

$$c^s = c^\infty - \Delta c \qquad 0 < r < a \qquad z = 0 \tag{3}$$

$$\frac{\partial c}{\partial z} = 0 \qquad r > a \qquad z = 0 \tag{4}$$

where Δc is the difference in concentration between infinity and the surface.

The solution to eqn. (2) is

$$c = c^\infty - \int_0^\infty f(\lambda) \exp(-\lambda z) J_0(\lambda r)\, dr \tag{5}$$

where the function $f(\lambda)$ must be chosen to satisfy eqns. (3) and (4); a term including $Y_0(\lambda r)$ in the general solution of eqn. (2) must be excluded as c remains finite for $r \to 0$. The integral (5) must be discontinuous at $r = a$ while eqn. (4) requires that

$$\left(\frac{\partial c}{\partial z}\right)_{z=0} = \int_0^\infty \lambda f(\lambda) J_0(\lambda r)\, d\lambda = 0 \tag{6}$$

for $r > a$ while for $r < a$ the gradient is arbitrary except that it cannot be zero.

The discontinuous integrals

$$\int_0^\infty \sin(\lambda a) J_0(\lambda r) \frac{d\lambda}{\lambda} \begin{cases} \frac{\pi}{2}, & r < a \\ \sin^{-1}\left(\frac{a}{r}\right) & r > a \end{cases} \tag{7}$$

associated with

$$\int_0^\infty \sin(\lambda a) J_0(\lambda r)\, d\lambda \begin{cases} \dfrac{1}{(a^2 - r^2)^{1/2}} & r < a \\ 0 & r > a \end{cases} \tag{8}$$

satisfy eqns. (3) and (4), respectively, provided

$$f(\lambda) = (2/\pi) \Delta c \sin(\lambda a) \tag{9}$$

i.e. we obtain the solution

$$c = c^\infty - \frac{2}{\pi}(c^\infty - c^s) \int_0^\infty \exp(-\lambda z) \sin(\lambda a) J_0(\lambda r) \frac{d\lambda}{\lambda} \tag{10}$$

We are interested in the total flux through the surface of the disk

$$F = 2\pi D \int_0^a \left(\frac{\partial c}{\partial z}\right)_{z=0} r\, dr = 4D(c^\infty - c^s) \int_0^a \int_0^\infty \sin(\lambda a) J_0(\lambda r) r\, dr\, d\lambda$$

$$= 4D(c^\infty - c^s) a \int_0^\infty \sin(\lambda a) J_1(\lambda a) \frac{d\lambda}{\lambda} = 4D(c^\infty - c^s) a \tag{11}$$

which, as we have noted above, is a well-known result.

THIN RINGS

It is most straightforward to derive expressions for the concentration distribution for conditions of constant flux into the ring [11,12]. The discontinuous integral

$$\int_0^\infty J_0(\lambda r)J_1(\lambda a)\mathrm{d}\lambda = \begin{cases} 0 & r > a \\ 1/2a & r = a \\ 1/a & r < a \end{cases} \tag{12}$$

shows that a disk source of strength Q (mol cm^{-2} s^{-1}) will give a concentration distribution

$$c = c^\infty + \frac{Qa}{D}\int_0^\infty \exp(-\lambda z)J_0(\lambda r)J_1(\lambda a)\frac{\mathrm{d}\lambda}{\lambda} \tag{13}$$

for the disk $0 < r < a$.

In order to obtain a corresponding expression for the ring $a < r < b$ we suppose that a disk sink of strength $-Q$ and radius b is superposed on the source (13). This sink generates a concentration distribution

$$c = -\frac{Qb}{D}\int_0^\infty \exp(-\lambda z)J_0(\lambda r)J_1(\lambda b)\frac{\mathrm{d}\lambda}{\lambda} \tag{14}$$

The effect of the superposed disks is to generate a flux distribution (flux to the surface $z = 0$)

$$\left.\begin{aligned} F &= 0 \quad r < a \\ F &= -Q \quad a < r < b \\ F &= 0 \quad r > b \end{aligned}\right\} \tag{15}$$

and the concentration distribution

$$c = c^\infty + \frac{Qa}{D}\int_0^\infty \exp(-\lambda z)J_0(\lambda r)J_1(\lambda a)\frac{\mathrm{d}\lambda}{\lambda} - \frac{Qb}{D}\int_0^\infty \exp(-\lambda z)J_0(\lambda r)J_1(\lambda b)\frac{\mathrm{d}\lambda}{\lambda} \tag{16}$$

We are especially interested in the concentration distribution over $z = 0$ as well as in the average concentration over the surface of the ring, c_{av}. We obtain

$$\begin{aligned} (c_r^s) &= c^\infty + \frac{Qa}{D}\int_0^\infty J_0(\lambda r)J_1(\lambda a)\frac{\mathrm{d}\lambda}{\lambda} - \frac{Qb}{D}\int_0^\infty J_0(\lambda r)J_1(\lambda b)\frac{\mathrm{d}\lambda}{\lambda} \\ &= c^\infty + \frac{Qa}{D}{}_2F_1\left\{\tfrac{1}{2};\ -\tfrac{1}{2};\ 1;\ \frac{r^2}{b^2}\frac{b^2}{a^2}\right\} - \frac{Qb}{D}{}_2F_1\left\{\tfrac{1}{2};\ -\tfrac{1}{2};\ 1;\ \frac{r^2}{b^2}\right\} \qquad \text{for } r < a \\ &= c^\infty + \frac{Qa^2}{2Dr}{}_2F_1\left\{\tfrac{1}{2};\ \tfrac{1}{2};\ 2;\ \frac{b^2}{r^2}\frac{a^2}{b^2}\right\} - \frac{Qb}{D}{}_2F_1\left\{\tfrac{1}{2};\ -\tfrac{1}{2};\ 1;\ \frac{r^2}{b^2}\right\} \qquad \text{for } a < r < b \\ &= c^\infty + \frac{Qa^2}{2Dr}{}_2F_1\left\{\tfrac{1}{2};\ \tfrac{1}{2};\ 2;\ \frac{b^2}{r^2}\frac{a^2}{b^2}\right\} - \frac{Qb^2}{2Dr}{}_2F_1\left\{\tfrac{1}{2};\ \tfrac{1}{2};\ 2;\ \frac{b^2}{r^2}\right\} \qquad \text{for } r > b \end{aligned} \tag{17}$$

where ${}_2F_1\{\ \}$ denotes the relevant hypergeometric functions. It is convenient to express eqn. (17) in terms of a dimensionless parameter

$$c_{z=0} = (c^\infty - c_r^s) D/Qb$$

$$= {}_2F_1\left\{\tfrac{1}{2};\ -\tfrac{1}{2};\ 1;\ \frac{r^2}{b^2}\right\} - \frac{a}{b}\,{}_2F_1\left\{\tfrac{1}{2};\ -\tfrac{1}{2};\ 1;\ \frac{r^2}{b^2}\frac{b^2}{a^2}\right\} \qquad \text{for } r < a$$

$$= {}_2F_1\left\{\tfrac{1}{2};\ -\tfrac{1}{2};\ 1;\ \frac{r^2}{b^2}\right\} - \frac{a^2}{2b^2}\frac{b}{r}\,{}_2F_1\left\{\tfrac{1}{2};\ \tfrac{1}{2};\ 2;\ \frac{b^2}{r^2}\frac{a^2}{b^2}\right\} \qquad \text{for } a < r < b$$

$$= \frac{b}{2r}\,{}_2F_1\left\{\tfrac{1}{2};\ \tfrac{1}{2};\ 2;\ \frac{b^2}{r^2}\right\} - \frac{a^2}{2b^2}\frac{b}{r}\,{}_2F_1\left\{\tfrac{1}{2};\ \tfrac{1}{2};\ 2;\ \frac{b^2}{r^2}\frac{a^2}{b^2}\right\} \qquad \text{for } r > b \tag{18}$$

Similarly we obtain for the average concentration over the surface of the ring

$$c_{av} = c^\infty + \frac{2Qa}{D(b^2-a^2)}\int_0^\infty\int_a^b J_0(\lambda r)J_1(\lambda a)r\,\mathrm{d}r\frac{\mathrm{d}\lambda}{\lambda}$$

$$- \frac{2Qb}{D(b^2-a^2)}\int_0^\infty\int_a^b J_0(\lambda r)J_1(\lambda b)r\,\mathrm{d}r\frac{\mathrm{d}\lambda}{\lambda}$$

$$= c^\infty + \frac{2Qa}{D(b^2-a^2)}\int_0^\infty J_1(\lambda a)\{bJ_1(\lambda b) - aJ_1(\lambda a)\}\frac{\mathrm{d}\lambda}{\lambda^2}$$

$$- \frac{2Qb}{D(b^2-a^2)}\int_0^\infty J_1(\lambda b)\{bJ_1(\lambda b) - aJ_1(\lambda a)\}\frac{\mathrm{d}\lambda}{\lambda^2}$$

$$= c^\infty - \frac{2Qb^2}{D(b^2-a^2)}\int_0^\infty J_1^2(\lambda b)\frac{\mathrm{d}\lambda}{\lambda^2} - \frac{2Qa^2}{D(b^2-a^2)}\int_0^\infty J_1^2(\lambda a)\frac{\mathrm{d}\lambda}{\lambda^2}$$

$$+ \frac{4Qab}{D(b^2-a^2)}\int_0^\infty J_1(\lambda a)J_1(\lambda b)\frac{\mathrm{d}\lambda}{\lambda^2}$$

$$= c^\infty - \frac{8Qb^3}{3\pi D(b^2-a^2)} - \frac{8Qa^3}{3\pi D(b^2-a^2)} + \frac{2Qa^2b}{D(b^2-a^2)}\,{}_2F_1\left\{\tfrac{1}{2};\ -\tfrac{1}{2};\ 2;\ \frac{a^2}{b^2}\right\} \tag{19}$$

DISCUSSION

The expressions derived here are exact: for example, eqn. (19) holds for all possible values of b/a and the known result for a disk [19]

$$c_{av} = c^\infty - 8Qb/3\pi D \tag{20}$$

is recovered on setting $a = 0$. Furthermore, the expression of the results in terms of hypergeometric functions is well suited to computer-based calculations. Figure 1 illustrates the relative concentration changes (expressed by the dimensionless parameter) over the range $0 < r < 3b$ at $z = 0$ for a disk ($b/a = \infty$) and for rings

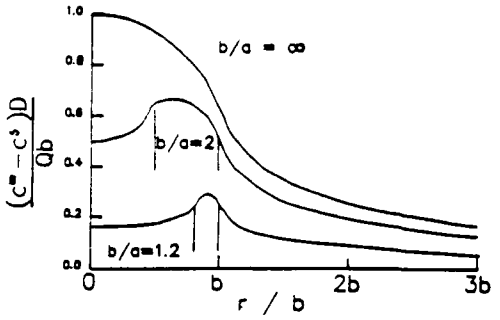

Fig. 1. Plot of the dimensionless concentration parameter $(c^{\infty} - c^{s})D/ab$ as a function of the radial position for a disk $(b/a = \infty)$ and for rings having the radius ratios $b/a = 2$ and 1.2, denotes the dimensions of the ring.

having $b/a = 2.0$ and 1.2, while Fig. 2 illustrates the concentration changes over the ring alone. The figures show that the concentration changes are markedly reduced as the thickness of the rings is decreased, a consequence of the enhanced mass transfer to the ring with decreasing ring thickness. At this time it is certainly feasible to prepare rings ≈ 10 nm thick on fibers of 10 μm radius giving $b/a \approx 1.001$. Figure 2 shows the consequent large increase of mass transfer to the ring. Decreasing ring thickness also leads to progressively more uniform concentrations over the surface of the ring which for $b/a = 1.001$ shows a maximum change of $\approx 5\%$ between the edges and the center.

Mass transfer coefficients to the surface of the ring can be derived in a variety of ways depending on the position at which the concentration is defined. A convenient choice is the average concentration [19] and setting $c_{Av} = 0$ we obtain

$$k_m = \frac{Q}{c^{\infty}} = \frac{D(b^2 - a^2)}{\frac{8b^3}{3\pi} - \frac{8a^3}{3\pi} - 2a^2 b_2 F_1\left\{\tfrac{1}{2}; -\tfrac{1}{2}; 2; \frac{a^2}{b^2}\right\}} \tag{21}$$

The enhancement of mass transfer to a thin ring as compared to that to a disk of the same radius is most conveniently expressed by the ratio

$$\left[\frac{(k_m)_{ring}}{(k_m)_{disk}}\right]_Q = \frac{8\frac{b}{a}\left(\frac{b^2}{a^2} - 1\right)}{3\pi\left[\frac{8}{3\pi}\left(\frac{b^3}{a^3} + 1\right) - \frac{2b}{a}{}_2F_1\left\{\tfrac{1}{2}; -\tfrac{1}{2}; 2; \frac{a^2}{b^2}\right\}\right]} \tag{22}$$

where the suffix Q denotes that we are considering conditions of constant flux over the surface of the electrode. Some values are listed in Table 1. An expression for the

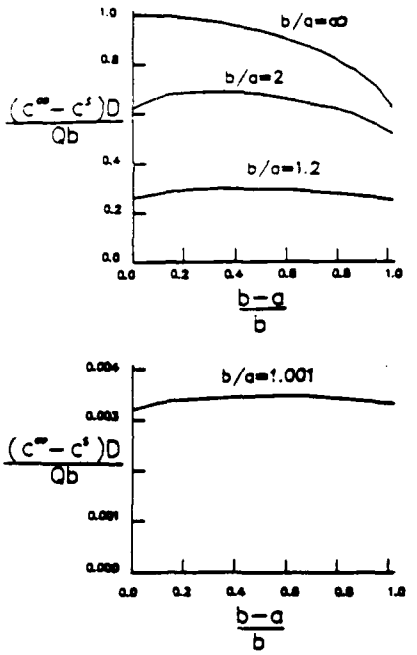

Fig. 2. Plot of the dimensionless concentration parameters $(c^{\infty} - c^{s})D/ab$ as a function of the radial position for a disk ($b/a = \infty$) and over the surface of rings having the radius ratios $b/a = 2$, 1.2 and 1.001.

average concentration change for constant flux conditions has also been given [12] from which we derive

$$\left[\frac{(k_m)_{ring}}{(k_m)_{disk}}\right]_Q = \frac{8}{3\left(1-\frac{a}{b}\right)\ln\left\{4e^{3/2}\left(\frac{1+a/b}{1-a/b}\right)\right\}} \tag{23}$$

The values calculated from eqn (23), Table 1, are remarkably close to the exact values even for relatively high b/a. It should be noted, however, that the definition of k_m in terms of the average concentration implies that when $c_{av} = 0$ some parts of the ring (or disk) will be at negative concentrations which is physically unsound. Alternative definitions based on the attainment of $c^s = 0$ at specific positions are illustrated in Table 1 by the values for $r = b$ and $r = (a + b)/2$, columns 4 and 5. These values are again exact i.e., there is no mathematical approximation but the differences between columns 2, 4 and 5 illustrate the difficulties of defining an appropriate model (see further below).

TABLE 1

The ratio $\left(\frac{(k_m)_{ring}}{(k_m)_{disk}}\right)_Q$ as a function of b/a and based on various definitions of the surface concentrations; comparison with values of $\left(\frac{(k_m)_{ring}}{(k_m)_{disk}}\right)_c$

b/a	$\frac{(k_m)_{ring}}{(k_m)_{disk}}$						
	eqn. (21)	eqn. (22) approx.	$c^1_{r=b}=0$	$c^2_{r=(a+b)/2}=0$	eqn. (24)	c^3 = const. cf. ref. 22	eqn. (25)
∞	1.000	not valid					
2	1.3514	1.3039	1.6733	1.284		1.3080	1.2747
1.5	1.7859	1.7795	2.126	1.710		1.7089	1.6892
1.25	2.6259	2.6229	3.017	2.528	1.992	2.4933	2.4824
1.2	3.0303	3.0279	3.448	2.922	2.319	2.8721	2.8633
1.125	4.1976	4.1962	4.694	4.059	3.586	3.9671	3.9614
1.091	5.3110	5.3100	5.833	5.145	4.777	5.0112	5.0078
1.021	17.396	17.347	18.721	16.956	19.372	16.376	16.345
1.010	32.887	32.887			40.242		30.858
1.005	60.358	60.358			80.086		56.573
1.001	254.52	254.52			398.84		238.08

The data in column 4 should correspond for low $(b-a)$ to values derived by our previous approximate analysis of the problem [11]; in that analysis a uniform ring sink of strength $Q(b-a)$ was placed at $r=(a+b)/2$ and the concentration was evaluated at $r=b$ (or a). This analysis led to the simple conclusion

$$k_m = 0.4694D/(b-a) \tag{24}$$

However, the values derived using eqn. (24) show that this approximation deviates markedly from the exact expression except for intermediate values of b/a; the use of eqn. (24) has been criticized [12].

Table 1 also gives data based on an exact calculation of the capacitance of a ring using triple integral equations [22]; the data in column 7 therefore correspond to constant concentration over the surface of the ring (and disk). Column 8 gives data based on an approximate analysis of this problem [23]

$$\left[\frac{(k_m)_{ring}}{(k_m)_{disk}}\right]_c = \frac{\pi^2}{4\left(1-\frac{a}{b}\right)\ln\left(16\left\{\frac{1+a/b}{1-a/b}\right\}\right)} \tag{25}$$

This theory has usually been regarded as being exact [11,12,24]; Table 1 shows that eqn. (25) is indeed remarkably accurate bearing in mind the nature of the approximations made. The deviations between the exact values for the exact analyses of the problem using the constant flux and constant concentration approximations, columns 2 and 7, illustrate the difficulties of choosing an appropriate model. The

constant flux approximation will apply to measurements at low overpotentials (especially for reactions which are relatively irreversible at these high rates of mass transfer) while the constant concentration approximation will hold at high overpotentials in the region of the limiting current plateau [11]. It is clear from the data in Figs. 1 and 2 as well as Table 1 that the best strategy at this stage of development of the subject is to use microring electrodes having the smallest attainable thickness since this will minimize the differences between the two approximations.

Although as we have shown previously [14], it is possible to measure fast electron transfer rate information in the steady state, it is clear that further enhancement in these measurements could be accomplished by using ac perturbation techniques; this work will be the subject of a forthcoming report.

ACKNOWLEDGEMENT

The authors thank the Office of Naval Research for support of this work.

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